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(21)Application number : 08-079830 (71)Applicant : POLYPLASTICS CO
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(54) PRODUCTION OF HIGH-MOLECULAR POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a high-molecular polymer which is a substantially linear polymer in high yields by using a specified catalyst and a specified oxidizing agent in synthesizing a high-molecular polymer by using an aromatic compound as the monomer and forming fresh C-C bonds.

SOLUTION: In producing an organic high-molecular polymer by using an aromatic compound as the monomer and forming fresh C-C bonds in an aromatic ring, the reaction is performed in the presence of a vanadium compound as the catalyst in an atmosphere of oxygen or air. The vanadium compound used is desirably an oxyvanadium complex, especially vanadyl acetylacetone [VO (acac)₂] which is highly active. Examples of the aromatic monomers used include benzene, substituted benzene derivatives, naphthalene and substituted naphthalene derivatives. The polymerization reaction is practiced in a solvent (desirably a polar solvent) containing an acid anhydride.

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(54) 【発明の名称】 高分子重合体の製造方法

(57) 【要約】

【課題】 高強度かつ優れた耐熱性を有する有機高分子材料を効率良く合成する方法を提供する。

【解決手段】 芳香族化合物をモノマーとし、新たな炭素-炭素結合の生成による高分子重合体を合成するにあたり、バナジウム酸化物を触媒とし、酸素を酸化剤として用いる。

【特許請求の範囲】

【請求項1】 芳香族化合物をモノマーとし、芳香環の新たな炭素-炭素結合の生成による有機高分子重合体を製造するにあたり、バナジウム化合物を触媒として用いることを特徴とする高分子重合体の製造方法。

【請求項2】 高分子重合体の製造にあたり、酸素または空気雰囲気下で反応を行う請求項1記載の高分子重合体の製造方法。

【請求項3】 バナジウム化合物がオキソバナジウム錯体である請求項1又は2記載の高分子重合体の製造方法。

【請求項4】 オキソバナジウム錯体がバナジルアセチルアセトナートVO(acac)₂である請求項3記載の高分子重合体の製造方法。

【請求項5】 モノマーがベンゼンあるいは置換基を有するベンゼン誘導体である請求項1～4の何れか1項記載の高分子重合体の製造方法。

【請求項6】 モノマーがアルコキシあるいはオキシアルキレン置換基を含むベンゼン誘導体である請求項5記載の高分子重合体の製造方法。

【請求項7】 アルコキシ置換基がブトキシ基である請求項6記載の高分子重合体の製造方法。

【請求項8】 モノマーがナフタレンあるいは置換基を有するナフタレン誘導体である請求項1～4の何れか1項記載の高分子重合体の製造方法。

【請求項9】 モノマーがアルコキシあるいはオキシアルキレン置換基を含むナフタレン誘導体である請求項8記載の高分子重合体の製造方法。

【請求項10】 モノマーがジナフチルアルキレンエーテルである請求項9記載の高分子重合体の製造方法。

【請求項11】 モノマーが1,5-ジ(1-ナフトキシ)ベンタンである請求項10記載の高分子重合体の製造方法。

【請求項12】 モノマーがジフェニルスルフィド、ジフェニルスルホキシドおよびジフェニルスルホンあるいはそれらの誘導体から選ばれる請求項8記載の高分子重合体の製造方法。

【請求項13】 重合反応が酸性化合物を含む溶媒中で行われることを特徴とする請求項1～12の何れか1項記載の高分子重合体の製造方法。

【請求項14】 重合反応が酸無水物を含む溶媒中で行われることを特徴とする請求項1～12の何れか1項記載の高分子重合体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高強度かつ優れた耐熱性を有する有機高分子材料の製造方法に関するものである。

【0002】

【従来の技術および本発明が解決しようとする課題】あ

る種の有機高分子材料はエンジニアリングプラスチックとして、従来金属材料、セラミック、ガラス、木材等が使用されてきた部分に代用され、これら従来材料に対して、加工性が優れていること、コストダウンが図れること等の特徴により急速に需要を伸ばしている。更に、プラスチック材料の特性である、加工のしやすさ、電気絶縁性、着色性、さらに添加剤、充填剤によりその性質を変化制御しやすいことなどにより、代替材料にとどまらず、独自の応用分野が開拓され、従来の材料では考えられなかつた部品製作等を可能とした。一方、エンジニアリングプラスチックの応用範囲が広がるにつれ、要求される特性のレベルも次第に高くなり、より高度な特性を有する新規な高分子材料の出現、工業化が期待されている。特に、ベンゼン環が鎖状に直結した構造を有する重合体は、その構造からして、極めて高い耐熱性と、機械特性とが予想され、その高分子量重合体の合成が試みられてきた。例えば、銅粉を触媒とする酸化反応による方法などが発表されている。しかしながら、重合体の諸特性、加工性などは重合体の構造、すなわち鎖状型あるいは屈曲型か、あるいは架橋型か、また分子量の大小に大きく依存し、所定の特性を達成するためにはこれらについても制御する必要がある。一般的に言えば、架橋型重合体は成形困難な場合が多く、また低分子量重合体はもろいなど機械特性に難点がある。また、芳香環における結合位置の異なる異性体の存在比が異なる場合には、その熱特性が一定しないなどの問題がある。芳香環が直結された重合体に関しては、これまでのところ、生成物の分子量が低く、かつ架橋構造を有するなど、成形性、機械特性において満足なものは未だ得られておらず、高分子量の鎖状重合体を安定して得る手法の確立が実用化のためには必須である。他方、ベンゼン環のみが直結した重合体、すなわちポリパラフェニレンにおいては、その構造からして、加工面での困難が予想され、置換ベンゼン構造を有するもの、他の化学結合との共重合化によって、その加工性を改善する検討も進められている。置換ベンゼンをモノマーとするものでは、本発明者らは既にハロゲン化鉄を酸化剤として用いる合成法を発明し、特許出願するに至った（特願平3-100849号）。しかし、この合成法では、ハロゲン化鉄が酸化剤として非循環的に用いられるため、工業的手法としてはまだ改善の余地があること、生成物の芳香環における結合位置に選択性が低いなどの課題があつた。

【0003】

【課題を解決するための手段】本発明者らは、高機能エンジニアリングプラスチック、具体的には芳香環が直結した構造を含む有機重合体を効率的に合成する手法の探索を進めてきたところ、バナジウム化合物を触媒とする酸化反応により、その生成物は結合の位置選択性が高く実質的に鎖状高分子で、かつ分子量が大きく、また高収率で重合反応を行うことができることを見出し、本発明

に至った。すなわち、本発明は、芳香族化合物をモノマーとし、新たな炭素-炭素結合の生成による高分子重合体を合成するにあたり、バナジウム化合物を触媒とし、酸素を酸化剤として用いることを特徴とする高分子重合体の製造方法に関する。

【0004】

【課題を解決するための手段】以下、本発明について詳細に説明する。本発明に用いられる上記の芳香族モノマーとは、芳香環の構造としてベンゼン、ナフタレン、アントラセン、フェナントレン、フルオレン等の骨格構造を含むものである。これらの芳香環は一般式 $Ar-(X-Ar)n$ ($n=0 \sim 6$) で表わされるように、単独あるいは2個以上の芳香環が結びつけられた構造を有するものを含む。ここで Ar は上記の芳香環を表わし、 X としては一般式 $-CnH2n-$ ($n=0 \sim 20$) で表わされるアルキレン、 $-OCnH2n-$ ($n=0 \sim 20$) で表わされるオキシアルキレン、 $-OCnH2nO-$ ($n=1 \sim 20$) で表わされるジオキシアルキレン、 $-(CnH2nO)n'$ ($n=1 \sim 20, n'=1 \sim 10$) で表わされるポリ(オキシアルキレン) 等の含酸素アルキレン、 $-S-$ 、 $-SO-$ 、 $-SO2-$ 等の含イオウ原子団がその例として挙げられる。より具体的には、例えばビフェニル、テルフエニル、ジフェニルメタン、1,2-ジフェニルエタン、1,3-ジフェニルプロパン、1,4-ジフェニルブタン、1,5-ジフェニルペンタン、1,6-ジフェニルヘキサン、1,8-ジフェニルオクタン、ジフェニルエーテル、ベンジルフェニルエーテル、2-フェネチルフェニルエーテル、ジ(2-フェネチル)エーテル、3-フェニルプロピルフェニルエーテル、ジ(3-フェニルプロピル)エーテル、1,2-ジフェノキシエタン、1,3-ジフェノキシプロパン、1,4-ジフェノキシブタン、1,5-ジフェノキシペンタン、1,6-ジフェノキシヘキサン、1,4-ジフェノキシベンゼン等、およびジフェニルスルフィド、ジフェニルスルフォキシド、ジフェニルスルホン等のベンゼン誘導体、ビナフチル、テルナフチル、ジナフチルメタン、1,2-ナフチルエタン、1,3-ジナフチルプロパン、1,4-ジナフチルブタン、1,5-ジナフチルペンタン、1,6-ジナフチルヘキサン、1,8-ジナフチルオクタン、ジナフチルエーテル、ベンジルフェニルエーテル、2-フェネチルフェニルエーテル、ジ(2-フェネチル)エーテル、3-フェニルプロピルフェニルエーテル、ジ(3-ナフチルプロピル)エーテル、1,2-ジナフトキシエタン、1,3-ジナフトキシプロパン、1,4-ジナフトキシブタン、1,5-ジナフトキシペンタン、1,6-ジナフトキシヘキサン、1,4-ジナフトキシベンゼン等、およびジナフチルスルフィド、ジナフチルスルホン等のナフタレン誘導体、さらに4,4'-ジ(フェノキシ)ジフェニルスルホン、4,4'-ジ(1-ナフトキシ)ジフェニルスルホン等も含まれる。これら芳香環には、反応性を高め、溶媒に対する溶解性を制御し、あるいは熱可塑性を制御し

て加工性を高める等の目的で、各種の置換基を導入してもよい。例えば、アルコキシル基を導入することにより、反応性を高め、また可溶媒性として溶液からのフィルム作製を容易にするなどの特性改良が可能となる。このような置換基の例としては、一般式 $CnH2n+10-$ ($n=1 \sim 12$) で表わされるアルコキシル基の他、アルキル基(一般式 $CnH2n+1-$ 、 $n=1 \sim 12$) 等が挙げられる。

【0005】以下では、モノマーとして1,4-ジアルコキシベンゼンを用いる場合を例にとり、本発明の内容を具体的に説明する。ベンゼンのアルコキシ置換体に対するバナジウム化合物触媒としては、含酸素バナジウム錯体、例えばバナジルアセチルアセトナート $V(OAc)_2$ 、バナジルビス(1-フェニル-2,4-ブタンジオアート)、バナジルテトラフェニルポルフィナート、しゅう酸バナジル $V(OO)_2$ 、硫酸バナジル $VOSO_4$ 、等を含むオキソバナジウム錯体が高触媒活性を有し、特にバナジルアセチルアセトナートが高活性を示す。添加される触媒の量は、モノマーに対して 0.1~100 モル%、活性および経済性のバランスの観点からは 1~10 モル% を用いるのが特に好ましい。重合反応は酸化剤としての純酸素または空気雰囲気下で行う。本重合反応においては、触媒であるバナジウム化合物が強酸性条件下、不均化する過程が含まれると考えられ、溶液中には強酸を添加する必要がある。ここで強酸としては、メタノスルホン酸、フルオロメタンスルホン酸、ジフルオロメタンスルホン酸、トリフルオロメタンスルホン酸、ベンゼンスルホン酸、アルキルベンゼンスルホン酸等が挙げられる。これら強酸の添加量は、バナジウム触媒の 0.1~100 倍モル量、好ましくは 1~10 倍モル量である。これら強酸は単独で、あるいは 2 種以上を混合して使用してもよい。バナジウム(IV) は強酸性条件下でバナジウム(III) やバナジウム(V) に不均化し、バナジウム(V) が直接の酸化活性種となる。他方バナジウム(III) も酸素によってバナジウム(IV) となり、循環的に触媒活性種となる。これら、酸の添加量に関しては、その添加量が少なければ活性が十分でなく、他方、過剰である時には好ましくない架橋反応など副反応が起こることを勘案して添加量を調整する必要がある。

【0006】上記の縮合反応の進行に伴い生成する水を除去するために、反応系には過剰の酸無水物を加えておく。ここで酸無水物とは各種の有機酸無水物、たとえば無水トリフルオロ酢酸、無水トリクロロ酢酸、無水フルオロ酢酸、無水クロロ酢酸、無水ジクロロ酢酸、無水ジフルオロ酢酸であり、これらは単独で、あるいは混合して用いられる。その添加量に関しては、モノマーに対して 1 倍モル量以上必要であるが、上限に関しては特に規定されない。溶媒は、モノマーおよび触媒、上記の酸を溶解しやすいという点から極性溶媒が一般的であり、かつ重合反応に不活性である化合物から選ばれる。用いられる極性溶媒の例としては、ジクロロメタン、1,2-ジ

クロロエタン、ニトロベンゼン、ジニトロベンゼン、ジメチルスルホキシド、ジメチルホルムアミド等が挙げられる。上記の重合反応温度は特に限定されず、通常室温にて反応は行われるが、必要により加温してもよい。

【0007】

【発明の効果】本発明によれば、機械的、耐熱性に優れた芳香族系高分子重合体を安価に製造することができ、このようにして製造された高分子重合体は高強度かつ耐熱性に優れた成形物、繊維あるいはフィラー、フィルムとしての応用が期待される。

【0008】

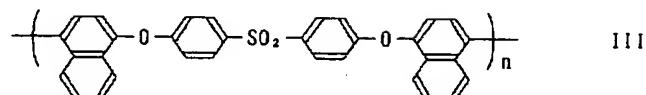
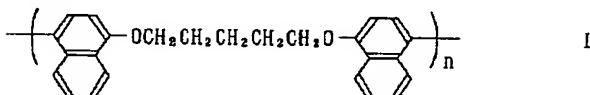
【実施例】以下に、実施例を挙げて本発明を具体的に説明するが、本発明はこれらの実施例により何ら限定されるものではない。

実施例1

二口フラスコに酸素供給管とセプタムキャップを取り付け、この中に0.66gのバナジルアセチルアセトナートを入れた後、酸素にてフラスコ内を置換する。引き続きこのフラスコ内に50mlのニトロベンゼン、13.9mlの無水トリフルオロ酢酸、0.44mlのトリフルオロメタンスルホン酸をセプタムキャップを通して添加し、1時間ほど攪拌する。しかる後、0.1リットルのニトロベンゼンに溶かした17.8gの1,5-ジ(1-ナフトキシ)ペンタンを添加し、室温にて15時間攪拌した。反応物は5%塩酸を含む5リットルのメタノール中に注ぎ、沈澱物を回収した。沈澱物はクロロホルムからメタノールへの再沈澱法により精製した。收率は100%であった。生成物の構造をNMRおよびIRにて調べたところ、下記式Iに示す重合体の生成が確認された。ゲルfiltration法で求めた生成重合体の重量平均分子量は53,000、数平均分子量は1,000であった。また熱重量分析法で求めた熱分解温度は窒素中で395°C、空气中で380°Cであった。DSCにて求めたガラス転移温度は142°Cであった。

【0009】

【化1】



【0014】実施例4

実施例1において純酸素に替えて、空気を流通させながら実施例1の手順に従い、重合を行ったところ実施例1と同様の結果を得た。ただし、実施例1に比較し反応速度は若干遅く、重合時間は20時間とした。

【0015】実施例5

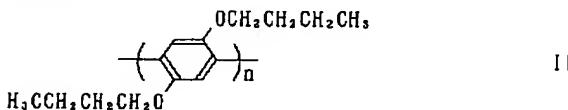
実施例2において純酸素に替えて、空気を流通させなが

【0010】実施例2

実施例1に示す如きフラスコ中に、1.99gのバナジルアセチルアセトナートを入れ、フラスコ内を酸素にて置換する。しかる後、30mlの1,2-ジクロロエタン、27.8mlの無水トリフルオロ酢酸、0.66gのトリフルオロメタンスルホン酸を加え、1時間ほど攪拌する。しかる後、70mlの1,2-ジクロロエタンに溶かした22.2gの1,4-ジ-*n*-ブトキシベンゼンを加え、室温にて20時間攪拌した。生成物は実施例1のごとく、回収、精製した。NMRおよびIR法、元素分析により求めた生成物の構造は下記式IIに示すものがほぼ100%選択的にできていることが分かった。生成重合体の重量平均および数平均分子量は各々30,000、12,000、10%熱分解温度は窒素中で385°Cであった。

【0011】

【化2】



【0012】実施例3

実施例1に示す反応容器中、25.1gの4,4'-ジ(1-ナフトキシ)ジフェニルスルホン、1.32gのバナジルアセチルアセトナート、13.9mlの無水トリフルオロ酢酸、0.88mlのトリフルオロメタンスルホン酸、および150mlのニトロベンゼンを用い、室温にて、実施例1の手順に従い、重合を行った。生成物はアセトンとメタノールにより、再結晶法にて精製し、100%の收率で重合体を得た。生成物の構造をIRおよび元素分析で決定したところ、下記式IIIに示す重合体であることが分かった。生成重合体の重量平均および数平均分子量は各々6,400、3,500であった。

【0013】

【化3】

ら実施例2の手順に従い、重合を行ったところ実施例2と同様の結果を得た。ただし、実施例2に比較し反応速度は若干遅く、重合時間は30時間とした。

【0016】実施例6

実施例3において純酸素に替えて、空気を流通させながら実施例3の手順に従い、重合を行ったところ実施例3と同様の結果を得た。ただし、実施例3に比較し反応速

度は若干遅く、重合時間は40時間とした。

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 08-079830 (71)Applicant : POLYPLASTICS CO

(22)Date of filing : 02.04.1996 (72)Inventor : UEDA MITSURU

(54) PRODUCTION OF HIGH-MOLECULAR POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a high-molecular polymer which is a substantially linear polymer in high yields by using a specified catalyst and a specified oxidizing agent in synthesizing a high-molecular polymer by using an aromatic compound as the monomer and forming fresh C-C bonds.

SOLUTION: In producing an organic high-molecular polymer by using an aromatic compound as the monomer and forming fresh C-C bonds in an aromatic ring, the reaction is performed in the presence of a vanadium compound as the catalyst in an atmosphere of oxygen or air. The vanadium compound used is desirably an oxyvanadium complex, especially vanadyl acetylacetone [VO (acac)₂] which is highly active. Examples of the aromatic monomers used include benzene, substituted benzene derivatives, naphthalene and substituted naphthalene derivatives. The polymerization reaction is practiced in a solvent (desirably a polar solvent) containing an acid anhydride.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the giant-molecule polymer which is characterized by using a vanadium compound as a catalyst in making an aromatic compound into a monomer and manufacturing the organic giant-molecule polymer by generation of the new carbon-carbon bonding of a ring.

[Claim 2] The manufacture approach of the macromolecule polymer according to claim 1 which reacts under oxygen or an air ambient atmosphere in manufacture of a macromolecule polymer.

[Claim 3] The manufacture approach of a macromolecule polymer according to claim 1 or 2 that a vanadium compound is an oxo-vanadium complex.

[Claim 4] an oxo-vanadium complex -- vanadyl acetylacetonato VO(acac) 2 it is -- the manufacture approach of a macromolecule polymer according to claim 3.

[Claim 5] The manufacture approach of the macromolecule polymer of claim 1-4 which is the benzene derivative with which a monomer has benzene or a substituent given in any 1 term.

[Claim 6] For alkoxy ******, a monomer is the manufacture approach of a macromolecule polymer according to claim 5 of being a benzene derivative containing an oxy-alkylene substituent.

[Claim 7] The manufacture approach of a macromolecule polymer according to claim 6 that an alkoxy substituent is a butoxy radical.

[Claim 8] The manufacture approach of the macromolecule polymer of claim 1-4 which is the naphthalene derivative with which a monomer has naphthalene or a substituent given in any 1 term.

[Claim 9] For alkoxy ******, a monomer is the manufacture approach of a macromolecule polymer according to claim 8 of being a naphthalene derivative containing an oxy-alkylene substituent.

[Claim 10] The manufacture approach of a macromolecule polymer according to claim 9 that a monomer is the dinaphthyl alkylene ether.

[Claim 11] The manufacture approach of a macromolecule polymer according to claim 10 that a monomer is 1 and 5-JI (1-naphthoxy) pentane.

[Claim 12] The manufacture approach of a macromolecule polymer according to claim 8 that a monomer is chosen from a diphenyl sulfide, a diphenyl sulfoxide and diphenylsulfone, or those derivatives.

[Claim 13] The manufacture approach of the macromolecule polymer of claim 1-12 characterized by performing a polymerization reaction in the solvent containing an acid compound given in any 1 term.

[Claim 14] The manufacture approach of the macromolecule polymer of claim 1-12 characterized by performing a polymerization reaction in the solvent containing an acid anhydride given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the manufacture approach of the organic polymeric materials which have high intensity and the outstanding thermal resistance.

[0002]

[The technical problem which a Prior art and this invention tend to solve] The part for which a metallic material, a ceramic, glass, wood, etc. have been used conventionally is substituted for a certain kind of organic polymeric materials as engineering plastics, and need is quickly developed according to the descriptions, like that workability is excellent and a cost cut can be aimed at to the ingredient conventionally [these]. Furthermore, it did not remain in alternate material in the ease of carrying out of processing which is the property of plastic material electric insulation, coloring nature, by being further easy to carry out change control of the property with an additive and a bulking agent, etc., but the original applicable field was reclaimed, and components manufacture which was not considered was enabled with the conventional ingredient. On the other hand, the level of the property demanded also becomes high gradually and the appearance of the new polymeric materials which have a more advanced property, and industrialization are expected as the application range of engineering plastics spreads. Thermal resistance especially with the polymer very expensive [considering the structure] which has the structure which the benzene ring linked directly in the shape of a chain, and a mechanical characteristic were expected, and composition of the amount polymer of macromolecules has been tried. For example, the approach by the oxidation reaction which makes copper powder a catalyst etc. is announced. however, many properties of a polymer, workability, etc. -- the structure, i.e., shape type of a chain, of a polymer -- or a crookedness mold or a bridge formation mold -- moreover, it is greatly dependent on the size of molecular weight, and in order to attain a predetermined property, it is necessary to control also about these Speaking generally, a bridge formation mold polymer's being difficult to fabricate in many cases, and a low-molecular-weight polymer has a difficulty in a mechanical characteristic, such as being weak. Moreover, when the abundance ratios of the isomer with which the joint locations in a ring differ differ, there is a problem that the heat characteristic is not fixed etc. It is indispensable in order for establishment of the technique which a satisfactory thing is not yet obtained, but is stabilized in the chain polymer of the amount of macromolecules in a moldability, such as the molecular weight of a product being low and having the structure of cross linkage an old place, and a mechanical characteristic, and is acquired about the polymer with which the ring was linked directly to be utilization. On the other hand, in the polymer which only the benzene ring linked directly, i.e., poly para-phenylene, considering the structure, the difficulty in respect of processing is expected and examination which improves the workability is also advanced by copolymerization-ization with what has permutation benzene structure, and other chemical bonds. In what makes permutation benzene a monomer, this invention persons invent the synthesis method which already uses halogenation iron as an oxidizer, and came to do patent application (Japanese Patent Application No. No. 100849 [three to]). However, in this synthesis method, since halogenation iron was acyclically used as an oxidizer, technical problems, like selectivity is low were in that there is still room of an improvement as the industrial technique, and the joint location in the ring of a product.

[0003]

[Means for Solving the Problem] The place where this invention persons have advanced retrieval of the technique of compounding efficiently an organic polymer including highly efficient engineering plastics and the structure which the ring specifically linked directly, by the oxidation reaction which makes a vanadium compound a catalyst, the site selectivity of association was a chain macromolecule substantially highly, the product had large molecular weight, and it resulted that a polymerization reaction could be performed by high yield in a header and this invention. That is, in making an aromatic compound into a monomer and compounding the giant-molecule polymer by generation of new carbon-carbon bonding, this invention relates to the manufacture approach of the giant-molecule polymer which makes a vanadium compound a catalyst and is characterized by using oxygen as an oxidizer.

[0004]

[Means for Solving the Problem] Hereafter, this invention is explained to a detail. The above-mentioned aromatic series monomer used for this invention includes skeletal structures, such as benzene, naphthalene, an anthracene, a phenanthrene, and a fluorene, as structure of a ring. these rings -- general formula it is independent as expressed with Ar-(X-Ar) n and (n=0-6) -- it is -- what has the structure where two or more rings were tied up is included. Ar expresses the above-mentioned ring and is X here. It is a general formula if it carries out. Alkylene expressed with -CnH2n- (n =0-20), - The oxy-alkylene expressed with OCnH2n- (n=0-20), - The dioxy alkylene expressed with OCnH2nO- (n =1-20), - oxygenated alkynes, such as Pori (oxy-alkylene) expressed with CnH2nOn'- (n=1-20, n'=1-10), -S-, -SO-, and -SO2- etc. -- a ** sulfur atomic group is mentioned as the example. More specifically For example, a biphenyl, a terphenyl, diphenylmethane, 1, 2-bibenzyl, 1, 3-diphenyl propane, 1, 4-diphenyl butane, 1, 5-diphenyl pentane, 1, 6-diphenyl hexane, 1, 8-diphenyl octane, Diphenyl ether, benzyl phenyl ether, 2-phenethyl phenyl ether, The JI (2-phenethyl) ether, 3-phenylpropyl phenyl ether, The JI (3-phenylpropyl) ether, 1, 2-JIFENOKISHI ethane, 1, 3-JIFENOKISHI propane, 1, 4-JIFENOKISHI butane, 1, 5-JIFENOKISHI pentane, 1, 6- JIFENOKISHI hexane, 1, 4-JIFENOKISHI benzene, etc., And benzene derivatives, such as a diphenyl sulfide, diphenyl sulfoxide, and diphenylsulfone, Binaphthyl, TERUNAFUCHIRU, dinaphthyl methane, 1, 2-naphthyl ethane, 1, 3-dinaphthyl propane, 1, 4-dinaphthyl butane, 1, 5-dinaphthyl pentane, 1, 6-dinaphthyl hexane, 1, 8-dinaphthyl octane, the dinaphthyl ether, Benzyl phenyl ether, 2-phenethyl phenyl ether, the JI (2-phenethyl) ether, 3-phenylpropyl phenyl ether, the JI (3-naphthyl propyl) ether, 1, 2-JINAFUTOKISHI ethane, 1, 3-JINAFUTOKISHI propane, 1, 4- JINAFUTOKISHI butane, 1, 5-JINAFUTOKISHI pentane, 1, 6-JINAFUTOKISHI hexane, Dinaphthyl sulfides, such as 1 and 4-JINAFUTOKISHI benzene, Naphthalene derivatives, such as dinaphthyl sulfoxide and a dinaphthyl sulfone, further 4, - JI (phenoxy) diphenylsulfone, and 4 '4, 4'-JI (1-naphthoxy) diphenylsulfone, etc. are contained. Reactivity may be raised to these rings, and the solubility over a solvent may be controlled to them, or thermoplasticity may be controlled to them, and various kinds of substituents may be introduced into them for the purpose, such as raising workability. For example, by introducing an alkoxy group, reactivity is raised and property amelioration of making film production from a solution easy as good solvent nature is attained. As an example of such a substituent, it is a general formula. An alkyl group (general formula CnH2n+1-, n=1-12) besides the alkoxy group expressed with CnH2n+1O- (n=1-12) etc. is mentioned.

[0005] Below, the case where 1 and 4-dialkoxy benzene is used as a monomer is taken for an example, and the contents of this invention are explained concretely. as the vanadium compound catalyst over the alkoxy substitution product of benzene -- the oxygenated vanadium complex VO(acac)₂, for example, vanadyl acetylacetato, a vanadyl screw (the 1-phenyl -2, 4-butane JIOATO), vanadyl tetra-phenyl PORUFINATO, oxalic acid vanadyl VO(COO)₂, and vanadyl sulfate VOSO₄ etc. -- the included oxo-vanadium complex has high catalytic activity, and especially vanadyl acetylacetato shows high activity. The amount of the catalyst added receives a monomer. 0.1-100 It is desirable especially to use 1-10-mol % from a viewpoint of the balance of mol%, activity, and economical efficiency. A polymerization reaction is performed under the pure oxygen as an oxidizer, or an air ambient atmosphere. In this polymerization reaction, under a strong acid nature condition, the vanadium compound which is a catalyst is considered that the process in which it dismutates is included, and needs to add strong acid in a solution. As strong acid, methansulfonic acid, fluoro methansulfonic acid, difluoro methansulfonic acid, trifluoro methansulfonic acid,

benzenesulfonic acid, alkylbenzene sulfonic acid, etc. are mentioned here. the addition of these strong acid -- vanadium catalyst 0.1-100 twice molar quantity -- it is one to 10 time molar quantity preferably. These strong acid is independent, or may mix and use two or more sorts. Vanadium (IV) is vanadium (III) under strong acid nature conditions. And it dismutates to vanadium (V) and vanadium (V) serves as direct oxidation active species. By oxygen, another side vanadium (III) also turns into vanadium (IV), and serves as a catalytic activity kind cyclically. If there are few the additions, activity is not enough, and about the addition of these acids, it is necessary to take into consideration that side reaction, such as another side and crosslinking reaction which is not desirable when superfluous, occurs, and to adjust an addition.

[0006] In order to remove the water generated with advance of the above-mentioned condensation reaction, the superfluous acid anhydride is added to the system of reaction. It is the organic-acid anhydride of various kinds [acid anhydride], for example, anhydrous trifluoroacetic acid, an anhydrous trichloroacetic acid, anhydrous gifblaar poison, a chloroacetic anhydride, anhydrous dichloroacetic acid, and anhydrous difluoroacetic acid here, and is independent, or it mixes, and these are used. About the addition, to a monomer, although it is required more than 1 time molar quantity, an upper limit is not especially specified. The point of being easy to dissolve the above-mentioned acid to a monomer and a catalyst, and the polar solvent of a solvent are common, and it is chosen as a polymerization reaction from the compound which is inactive. As an example of the polar solvent used, dichloromethane, 1, 2-dichloroethane, a nitrobenzene, a dinitrobenzene, dimethyl sulfoxide, dimethylformamide, etc. are mentioned. Although especially the above-mentioned polymerization reaction temperature is not limited but a reaction is usually performed at a room temperature, you may warm as occasion demands.

[0007]

[Effect of the Invention] According to this invention, the aromatic series system macromolecule polymer excellent in thermal resistance can be manufactured cheaply, and the application as mechanical, the moldings the macromolecule polymer manufactured by doing in this way excelled [moldings] in high intensity and thermal resistance, fiber or a filler, and a film is expected.

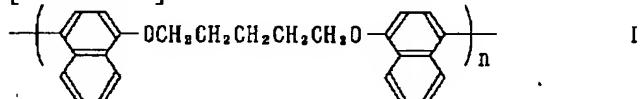
[0008]

[Example] Although an example is given to below and this invention is concretely explained to it, this invention is not limited at all by these examples.

After attaching oxygen supply tubing and a septum cap in an example 1 two-lot flask and putting in 0.66g vanadyl acetylacetone into this, the inside of a flask is permuted with oxygen. Succeedingly, in this flask, it adds through a septum cap and a 50ml nitrobenzene, 13.9ml anhydrous trifluoroacetic acid, and 0.44ml trifluoro methansulfonic acid are stirred for about 1 hour. After an appropriate time and 0.1 17.8g 1 and 5-JI (1-naphthoxy) pentane melted to the nitrobenzene of a liter was added, and it stirred at the room temperature for 15 hours. The reactant was poured out into the 5l. methanol which contains a hydrochloric acid 5%, and collected settling. Settling were refined by the method of reprecipitating a methanol from chloroform. Yield It was 100%. It is NMR about the structure of a product. And when investigated in IR, generation of the polymer shown in the following type I was checked. The weight average molecular weight of the generation polymer for which it asked by gel filtration technique was 53,000, and number average molecular weight was 11,000. Moreover, the pyrolysis temperature searched for by thermogravimetric analysis is in 395 ** and air in nitrogen. It was 380 degrees C. DSC Glass transition temperature for which it asked It was 142 degrees C.

[0009]

[Formula 1]

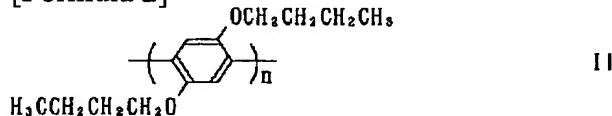


[0010] In the **** flask shown in example 2 example 1, 1.99g vanadyl acetylacetone is put in and the inside of a flask is permuted with oxygen. After an appropriate time, 30ml 1 and 2-dichloroethane, 27.8ml anhydrous trifluoroacetic acid, and 0.66g trifluoro methansulfonic acid are added, and it stirs for about 1 hour. After an appropriate time, the 22.2g 1 and 4-G n-butoxy benzene melted to 70ml 1 and 2-dichloroethane was added, and it stirred at the room temperature for 20

hours. The product was collected and refined like the example 1. NMR and the thing which shows the structure of the product for which it asked by the IR method and elemental analysis in the following type II -- almost -- It turned out that the selection target has done 100%. For the weighted mean and number average molecular weight of a generation polymer, 30,000 and 12,000 or 10% pyrolysis temperature are in nitrogen respectively. It was 385 degrees C.

[0011]

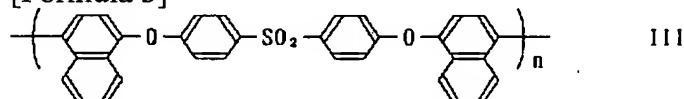
[Formula 2]



[0012] the inside of the reaction container shown in example 3 example 1, 25.1g 4 and 4'-JI (1-naphthoxy) diphenylsulfone, 1.32g vanadyl acetylacetonato, 13.9ml anhydrous trifluoroacetic acid, and 0.88ml trifluoro methansulfonic acid -- and -- According to the procedure of an example 1, the polymerization was performed at the room temperature using the 150ml nitrobenzene. an acetone and a methanol refine a product by the recrystallizing method -- the polymer was obtained with 100% of yield. When the structure of a product was determined by IR and elemental analysis, it is the following formula III. It turned out that it is the shown polymer. The weighted means and number average molecular weight of a generation polymer were 6,400 and 3,500 respectively.

[0013]

[Formula 3]



[0014] In example 4 example 1, it changed to pure oxygen, and when the polymerization was performed according to the procedure of an example 1, circulating air, the same result as an example 1 was obtained. However, as compared with the example 1, the reaction rate was slow a little, and polymerization time amount was made into 20 hours.

[0015] In example 5 example 2, it changed to pure oxygen, and when the polymerization was performed according to the procedure of an example 2, circulating air, the same result as an example 2 was obtained. However, as compared with the example 2, the reaction rate was slow a little, and polymerization time amount was made into 30 hours.

[0016] In example 6 example 3, it changed to pure oxygen, and when the polymerization was performed according to the procedure of an example 3, circulating air, the same result as an example 3 was obtained. However, as compared with the example 3, the reaction rate was slow a little, and polymerization time amount was made into 40 hours.

[Translation done.]